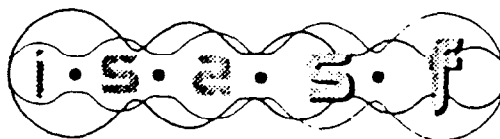International Society for the Advancement of Supercritical Fluids

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SYNTHETIC MODIFICATION OF OLEOCHEMICALS IN CRITICAL FLUIDS

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INTRODUCTION

The conversion of many lipid species to other useful oleochemical compounds can be readily accomplished in supercritical carbon dioxide ($SC\text{-}CO_2$) due to the relative high solubility of these compounds in dense CO_2. This factor coupled with the pressure dependence of reaction rate constants promotes rapid kinetic conversion of these moieties through adjustments of the compressed fluid's density. Testimony to this fact are the large number of different types of chemical reactions that have been successfully conducted in supercritical fluids [1-5], including hydrogenation [6,7], and lipase-based catalysis of oils/fats [8,9]. Studies conducted in our research group have demonstrated that esterifications, glycerolyses, and hydrolyses of vegetable oils can be run in $SC\text{-}CO_2$ and that hydrolyses of fats/oils can also be achieved using subcritical water.

Recently hydrogenation of oleochemicals has been explored by Harrod, et al. [10,11] and Tacke and coworkers [12,13]. These investigators have providing convincing evidence that hydrogenation of fats/oils and oleochemicals is feasible under supercritical conditions, using agents as $SC\text{-}CO_2$ and supercritical propane ($SC\text{-}C_3H_8$). Several patents [14,15] have been submitted/issued claiming uniqueness of the above potential processes, although the economic rationale and willingness of industry to accept these unusual approaches is still unknown. In addition, somewhat unconventional catalysts were used to perform the hydrogenation in small scale flow reactors.

In this study, we have extensively investigated the hydrogenation of fatty acid methyl esters (FAMES) of soybean oil using mixtures of hydrogen with $SC\text{-}CO_2$ or $SC\text{-}C_3H_8$. A novel experimental approach has been developed using commercially-available supercritical fluid extraction (SFE) instrumentation, and the reaction conditions have been optimized for a flow reactor. The derived product mixtures have been characterized using both gas (GC) and capillary supercritical fluid chromatography (SFC); the results indicating that there are advantages and disadvantages to using either the $H_2/SC\text{-}CO_2$ or $H_2/SC\text{-}C_3H_8$ systems. High yields of saturated alcohols are realized (approx. 90% steryl alcohol) at pressures and temperatures above 200 bar and 200°C, respectively. The reaction utilizes conventional hydrogenation catalysts and has been successfully coupled with enzymatic synthesis of the FAMES in $SC\text{-}CO_2$ to yield a two step, highly efficient reaction sequence for converting vegetable oils to saturated alcohol mixtures.

MATERIALS AND METHODS

The basic experimental apparatus for studying the hydrogenation of FAMES under supercritical conditions is shown in Fig. 1. The individual gases (fluids) were metered using a Brooks Series 5850E mass flow controller whose output was fed into a Parr Instruments Co. high pressure, stirred autoclave (1000 mL capacity) to assure homogeneity. The resultant binary fluid mixture was then compressed to the desired reaction pressure using a Haskel AGT-62/152 gas booster compressor and introduced into the reaction vessel containing either copper chromite catalyst E-406TU (Engelhard, Inc.) or chromium-free catalyst, T-4489 (United Catalysts, Inc.). The reaction cell was contained in the oven of an Applied Separations, Inc Spe-ed supercritical fluid extraction unit. The synthesized alcohols were collected after decompression of the binary fluid mixture through the micro metering valves on the Spe-ed unit. The product methanol was trapped in a condenser.

As shown in Fig. 1, the FAME feedstock was fed into the $H_2/SC-CO_2$ and H_2/C_3H_8 stream using a Isco Model 100DX syringe pump. The FAME-$H_2/SC-CO_2$ or -H_2/C_3H_8 mixture was then transported over the hydrogenation catalyst contained in one of several small volume reactor vessels (1 - 4.5 mL; 3 - 1 mL cells). For these experiments, a variety of Isco syringe pumps were utilized to deliver reagents (soybean oil, methanol, FAMES) as well as liquefied fluid (CO_2). For the initial hydrogenation studies, a welding-grade CO_2 was used in conjunction with hydrogen. Grade 4 (BOX Group, Inc.) or propane from the same source. In later experiments involving enzymatic synthesis of FAMES, SFC/SFE-Grade CO_2 from Air Products, Inc. was used and delivered via a cooled syringe pump. Soybean oil (refined, bleached, deodorized) was obtained from Riceland Industries; and the FAME feedstock with the exception of the enzymatically-synthesized product, from either Chemol Company or AG Environmental Products (SoyGold 100). The Novozym SP 435 was a product of Novo Nordisk.

The system used to study the sequential, two-step reaction conversion of soybean oil to fatty alcohol mixtures coupled a Isco SFX-2-10 extractor module with flanking Isco syringe pumps that were used to deliver the oil and methanol respectively into the SC-CO_2 prior to the reactor cell. Transesterification of soybean oil was accomplished using the conditions and a similar procedure described by Jackson and King [16]. Utilizing a pressure of 170 bar and temperature of 50 °C, a supported enzyme catalyst, Novozym SP 435 contained in a 10 mL reaction vessel, was employed in a small tubular reactor for the oil to FAME conversion. The resultant product was then transferred into the apparatus described in Fig. 1 using SC-CO_2 to the hydrogenation on the synthesized FAMES.

Gas chromatographic analysis of the resultant fatty alcohols or by-products, and the starting reactants (FAMES), utilized a HP-1 25m long, 250μm i.d., 0.25 μm film thickness column contained in a Hewlett Packard Model 6890 gas chromatograph. The supercritical fluid chromatographic (SFC) analysis of product/reactant mixtures from the enzyme synthesis step was accomplished using a Dionex Series 600 SFC containing a SB-Methyl-100, 10 m long column, 50 μm i.d., 0.25 μm film thickness [17].
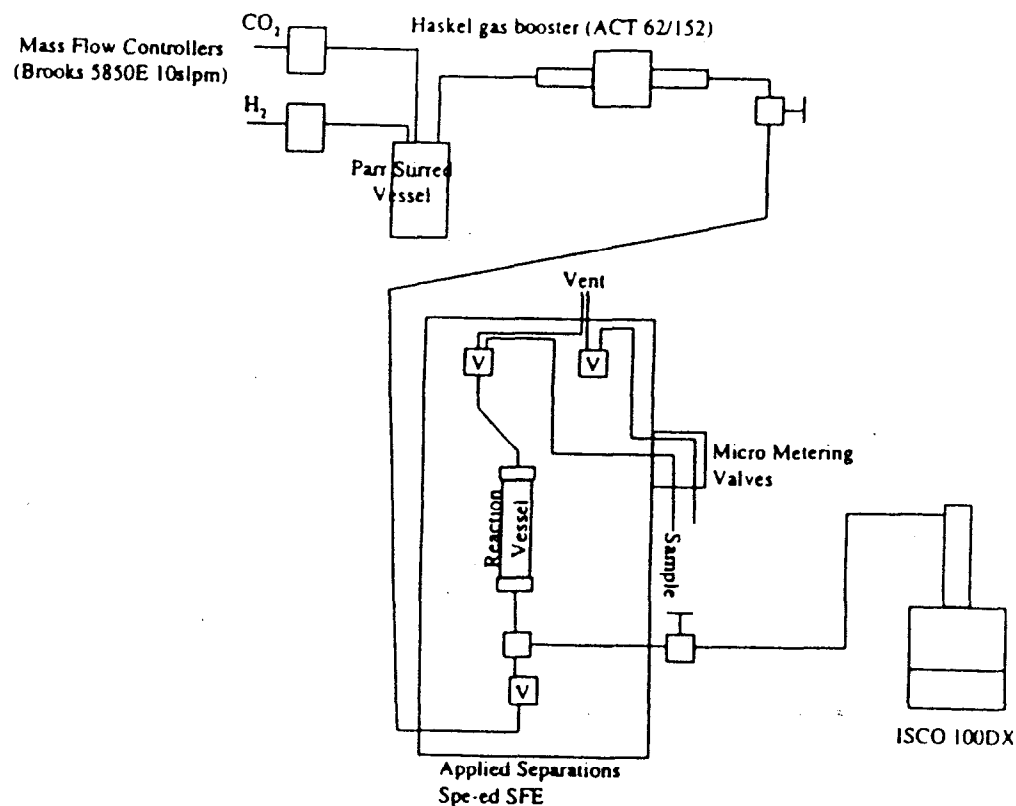
Figu

Tabl

Fluid

CO2
CO2
Propane
Propane

Figure 1. Reaction system for hydrogenating FAMES to alcohols using binary fluid mixtures of $H_2/SC\text{-}CO_2$ and H_2/C_3H_8.

Table 1. Range of experimental conditions investigated utilizing the system in Fig. 1 for hydrogenating FAMES to alcohols.

Fluid	Catalyst	Pressure (bar)	Temperature (°C)	Mole % H_2	Reaction time (s)	Substrate flow ($\mu L/min$)
CO_2	Copper chromite	150-250	210-250	10-25	4-9	25-50
CO_2	Chromium free	150-250	210-250	10-25	4-9	25-50
Propane	Copper chromite	150-250	210-250	10-25	4-9	50-250
Propane	Chromium free	150-250	210-250	10-25	4-9	50-250

RESULTS AND DISCUSSION

Table 1 lists the experimental range of parameters that were investigated in this study. These conditions were arrived at based on an experimental design program and preliminary experiments which helped focus the conditions which would be most promising for conducting hydrogenation of FAMES. Both types of hydrogenation catalysts were tested with the $H_2/SC\text{-}CO_2$ and $H_2/SC\text{-}C_3H_8$ mixtures over a pressure range of 150 - 250 bar and a temperature range of 210 - 250°C. The mole fraction of hydrogen in the $SC\text{-}CO_2$ and $SC\text{-}C_3H_8$ ranged from 0.10 - 0.25. Reaction times in reactor vessels ranged from 4 - 9 sec. while FAME feed for the $H_2/SC\text{-}CO_2$ system was 25-50 μL/min and 50 - 250 μL/min for the $H_2/SC\text{-}C_3H_8$ mixtures. The higher injection rate of FAMES into the $H_2/SC\text{-}C_3H_8$ system reflects the higher solubility of the FAMES in this particular solvent system.

A response surface graph showing the relationship between product yield, the mole fraction of H_2 in the two binary fluid mixtures, and the reaction temperature is plotted in Fig. 2 for the chromium-free catalyst system. It was found from earlier experiments that when varying the above parameters, a reaction pressure of 250 bar was necessary to produce high alcohol yields. Consequently the two plots in Figs. 2a and 3b were established for this reaction pressure. It should be noted however, that under certain conditions lower pressures produced acceptable yields ($\geq 96\%$) of fully hydrogenated alcohols; in fact in the case of propane, a pressure of 150 bar proved adequate under some conditions to yield high conversions of FAMES.

Inspection of Figs. 2a and 2b shows that at 25 mole % of H_2 in $SC\text{-}CO_2$, and a reaction temperature of 250°C, that the yield of alcohols is slightly greater than for the $H_2/SC\text{-}CO_2$ system under the same conditions. The reasons for this reduced conversion in C_3H_8 will be explained shortly, however the overall response surface for the H_2/C_3H_8 system indicates that high alcohol conversions can also be accomplished using lower mole fractions of hydrogen in propane than for the $H_2/SC\text{-}CO_2$ system (only approx. 50%). Response surfaces for the copper chromite catalyst follow similar trends; the $H_2/SC\text{-}CO_2$ outperforming the $H_2/SC\text{-}C_3H_8$ at 25 mole % H_2, however at 10 mole % H_2, both the $H_2/SC\text{-}CO_2$ and $H_2/SC\text{-}C_3H_8$ systems yield approximately 80 % conversion. This points out the importance of catalyst selection on the overall yield and required reaction conditions. All of the surface response plots for both binary fluid systems indicate the importance of the reaction temperature on alcohol yield in these "dilute" supercritical fluid solvent systems.

Figs. 3a and 3b are the gas chromatographic profiles of the hydrogenated product mixture derived from the reaction in the $H_2/SC\text{-}CO_2$ and $H_2/SC\text{-}C_3H_8$ systems, respectively; the peaks being identified by the retention time of standard compounds. The flame ionization detector (FID) response shows a high conversion (97.2 %) for the two principle hydrogenated fatty alcohols derivable from soybean oil; steryl and palmityl alcohols. Only trace levels of unconverted FAMES remain. By contrast, Fig. 3b corresponding to the product distribution obtained with the $H_2/SC\text{-}C_3H_8$ system, shows not only the appearance of the fatty alcohols, but significant amounts of $n\text{-}C_{16}$ and $n\text{-}C_{18}$
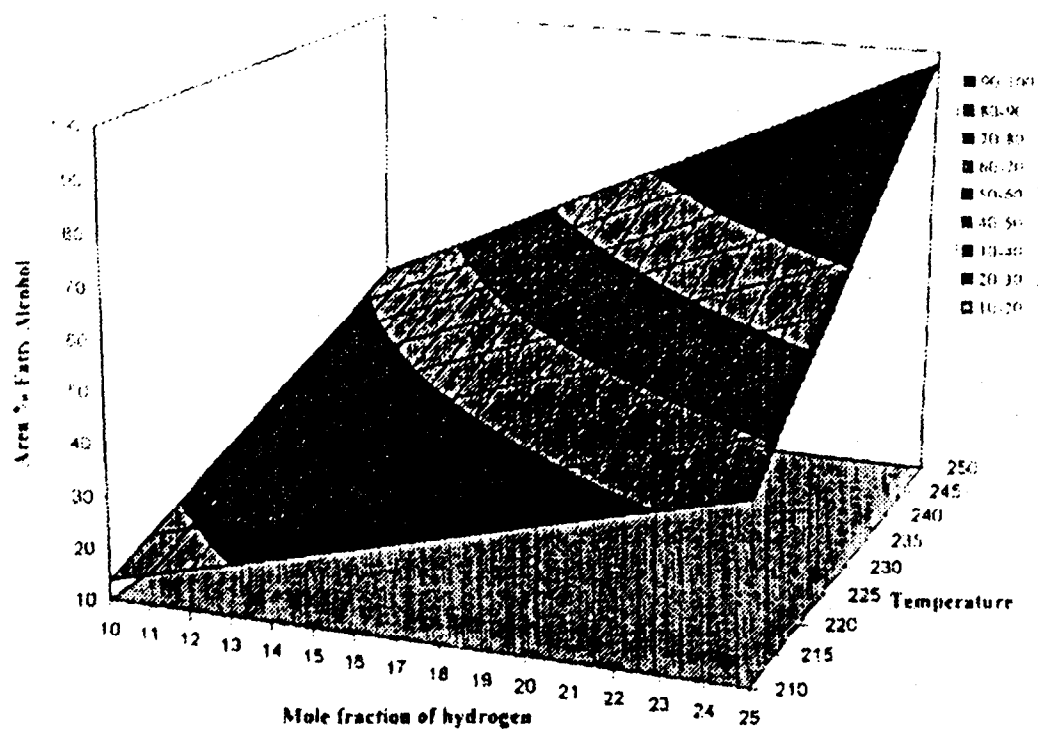
Figure 2a. Response surface for production of fatty alcohols in $H_2/SC\text{-}C_3H_7$ CO_x
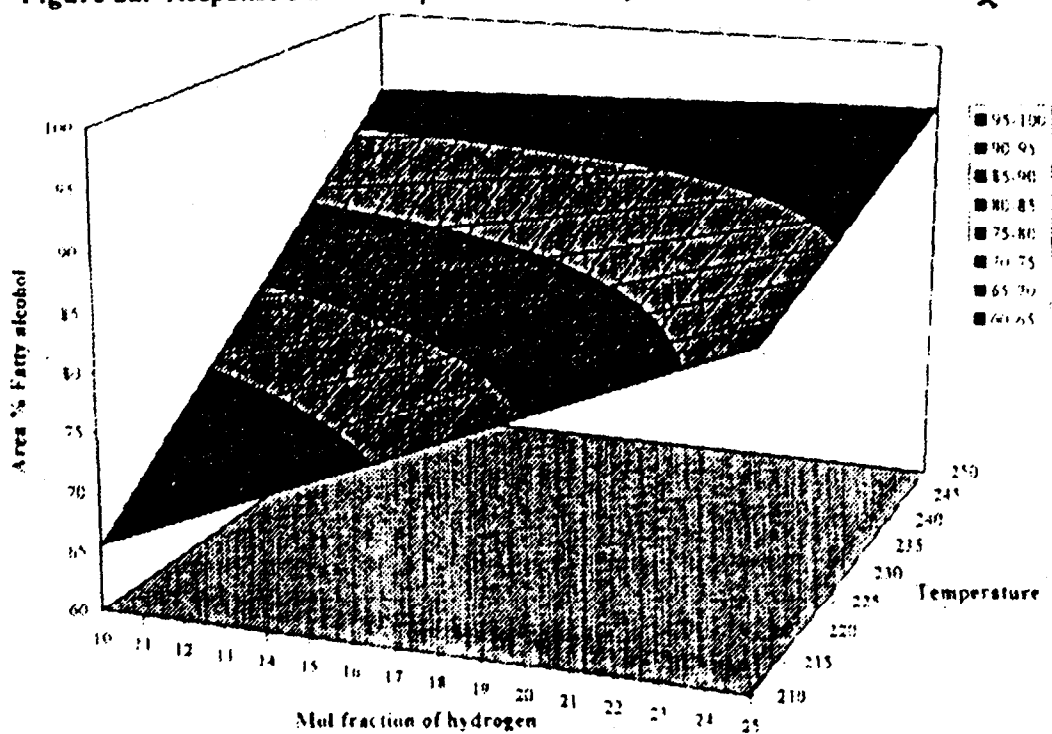

Figure 2b. Response surface for the production of fatty alcohols in $H_2/SC\text{-}CO_2$ C_3H_8

alkane by-product [18, 19]. Here the two alcohols constitute 95 % of the product mixture while the n-alkane components total 4.6 %. Both of these product mixtures were generated at 250 bar, 250°C, 25 mole % H_2 and a reaction time of 9 sec using the chromium-free catalyst. A similar trend is also noted for the two binary gas mixtures under similar conditions for the copper chromite catalyst. This observation than accounts for the limiting hydrogenated alcohol yields obtained using the $H_2/SC-C_3H_8$ system.

Therefore there are tradeoffs in employing the $H_2/SC-C_3H_8$ versus the $H_2/SC-CO_2$ system; one system allows the highest potential conversion to alcohols to be achieved, while the other binary fluid mixture (H_2/C_3H_8) permits a higher throughput to be achieved. The rate of conversion of FAMES to alcohols is higher for the $H_2/SC-C_3H_8$ mixture than for the $H_2/SC-CO_2$ binary fluid, due in part to the higher solubility of FAMES in the former mixture, thereby permitting more substrate to be solvated in the binary fluid mixture. This than allows more FAME to be transported over the catalyst bed yielding more alcohol/unit of time. For example, 3 times more alcohol can be synthesized in the $H_2/SC-C_3H_8$ mixture in 2/3 of the time than can be accomplished under similar conditions in the $H_2/SC-CO_2$ mixture.

Fig. 4 illustrates the GC product mixture that is obtained using enzymatic catalysis to form the FAMES from soybean oil followed by consecutive hydrogenation over the chromium-free catalyst. The result is a high conversion to alcohols (96.5 % yield) with only traces of the original FAMES detected in the chromatogram. This demonstrates that the two-stage reaction sequence works using $SC-CO_2$ as a process medium. The hydrogenation was conducted using the same conditions noted for Fig. 3a. The conversion of the soybean oil over Novozym SP 435 was followed using capillary SFC, which indicated that the reaction was complete; only C_{16} and C_{18} FAME appeared in the chromatogram.

CONCLUSIONS

The results of this study demonstrate the feasibility of continuously hydrogenating fatty acid methyl esters from vegetable oil resources using a "green" synthesis approach. The described study was accomplished using analytical scale equipment and such "green" reagents as carbon dioxide, a lipase catalyst, and a chromium-free catalyst for the hydrogenation step. For the hydrogenation stage, the rapid conversion rate of the starting FAME substrate suggests a potentially high production rate if the process is scaled up. It is interesting to note that these "supercritical" hydrogenations are dependent on the choice of catalyst with respect to optimizing product yield and distribution. Since one of the products from the hydrogenation step is methanol, the possibility exists of recycling this moiety back to the transesterification stage as a reactant for forming more FAMES. FAMES as opposed to neat fatty acids should be viewed as key synthetic starting materials for the synthesis of oleochemicals in critical fluid media, since they minimize corrosion of reactor materials and attrition of the catalyst. The resultant fatty alcohol mixtures from the above reaction sequence are potential feedstock for synthesis in industry for surfactant production [20], and could be fractionated further, perhaps using supercritical fluid fractionation, to produce even higher purity oleophilic alcohols.
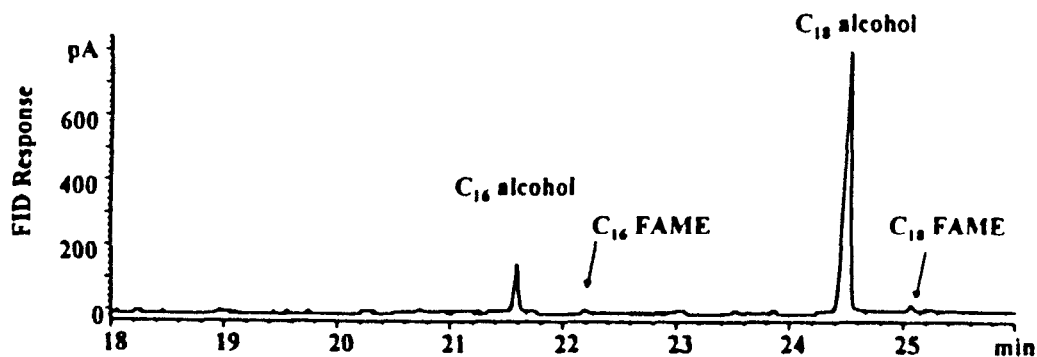
Figure 3a GC profile of products from critical fluid hydrogenation (H₂/SC-CO₂) of FAMES using Cr-free catalyst.
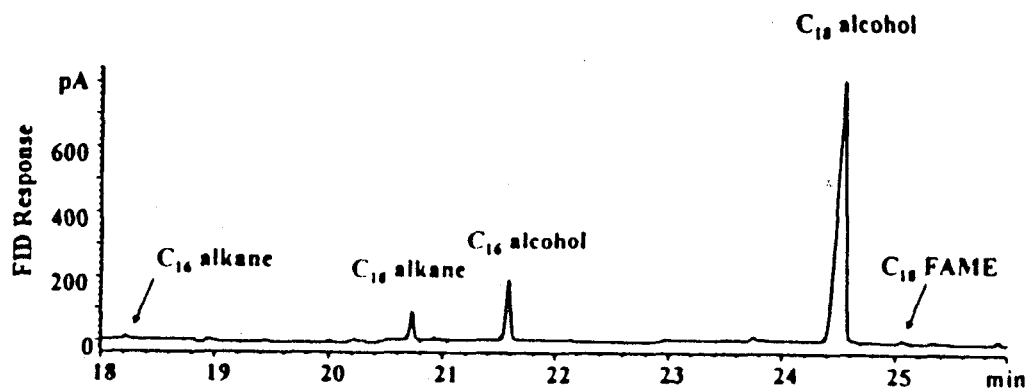

Figure 3b GC profile of products from critical fluid hydrogenation (H₂/SC-CO₂) of FAMES using Cr-free catalyst.
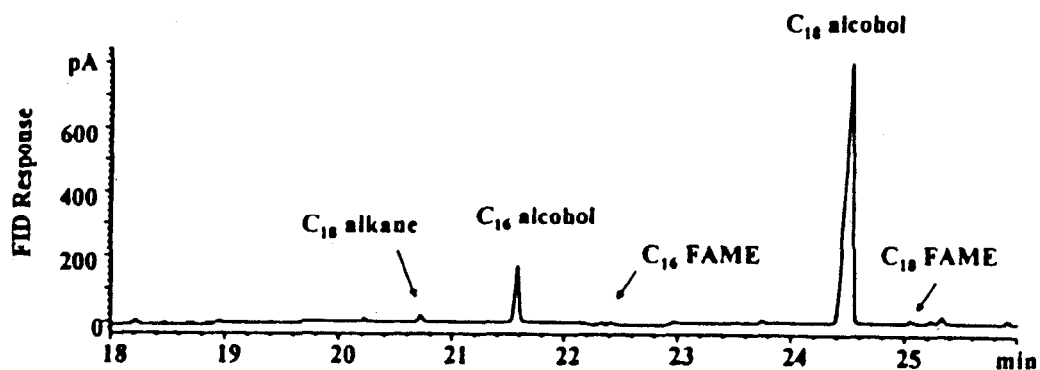

Figure 4 GC profile of products from SFR (transesterification)/SFR (hydrogenation - H₂/SC-CO₂) of soybean oil.

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